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Nanostructured Mn-Doped and undoped CuO thin films-PEC studies

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Abstract : The photoelectrochemical properties of copper oxide thin film (p-type) on the SnO_2 : F coated glass (conducting glass) prepared by spray pyrolysis has been investigated as a function dopant and pH of electrolyte. X-ray diffractogram pattern of thin films confirm the cupric oxide (CuO) phase. Mn-doped samples exhibited decreased photoelectrochemical response as compared to undoped CuO. The onset of photocurrent in undoped CuO is at ~120 mV, while in Mn doped CuO films it is ~375 mV. The observed reverse effect of Mn-doping on the photoelectrochemical response of the films, can be attributed to the possible neutralization of naturally occurring majority charge carriers (holes) present in undoped copper oxide with the extra electrons furnished by the dopant Mn atoms, particularly, from their d orbitals. Better photoresponse has been observed at pH 13.

Keywords : Photoelectrochemical properties, cupric oxide, conducting glass, spray pyrolysis

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1. Introduction

Photoelectrochemical (PEC) cells, with active semiconductor electrolyte junction, are considered to be efficient solar energy harvestor, and intensive research is going on to use such systems in photosplitting of water for the production of hydrogen – a much cleaner substitute of fossil fuels. An ideal semiconductor for this kind of work should have a band gap in the range of 1.7–2.1 eV (a few tenth of an electron volt larger than theoretical minimum value of 1.23 eV needed for splitting of water), should be abundantly and economically available and should be stable in electrolyte. Fujishima and Honda, in 1972 [1] reported, for the first time, the possibility of using TiO_2 in PEC splitting of water, but, on account of large band gap of TiO_2 (3.1 eV), the conversion efficiency of solar energy was limited. After that a host of other semiconductors e.g. $SrTiO_3$ [2], $BaTiO_3$ [3] and SnO_2 [4], Fe_2O_3 [5], Si [6], GaAs [7], InP [8] and CdS [9] *etc.* have been investigated. However, desired results could not be achieved either due to large or small band gap or their instability in the electrolyte.

The present investigation deals with the study of copper oxide (CuO) thin film, prepared by spray-pyrolysis, as semiconductor electrode in PEC cell. Oxides of copper, Cu_2O having a direct band gap of about 2.1 eV [10, 11] and is therefore, strongly absorbing at wavelengths below 600 nm, CuO with band gap 1.21–1.51 eV [12, 13] is absorbing throughout the visible region. Besides this, the other reasons for selection of this material are its : (a) natural abundance, (b) low cost production processing, (c) non toxic nature and (d) stability and reasonably good electrical properties. The effect of dopant and its concentration and the pH of electrolyte on the photoelectrochemical conversion properties have been studied. The optical property, such as, band gap, phase identification, surface morphology have been studied using UV-Visible spectrophotometer, XRD and SEM, respectively.

2. Experimental technique

Copper oxide thin films were deposited on conducting glass (SnO_2 : F coated) substrates (TCO), by spraying 0.1 M precursor solution, prepared by dissolving $Cu(NO_3)_2.2.5H_2O$ (99.99+%, Aldrich) and the calculated amount of dopant $Mn(NO_3)_2.2H_2O$ (Aldrich) in double-distilled water. The films of copper oxide were deposited over existing coating of SnO_2 : F. The solution (pH ~3.5) was sprayed onto heated (temperature 350 ± 5°C) substrates of dimensions 4 cm × 2.5 cm. The detailed conditions for the spray deposition of copper oxide films have been summarized in Table 1. Before spraying, nearly one third length of the substrate was covered by an aluminium foil. The details of experimental set-up is described elsewhere [14].

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Table 1 Conditions for the spray deposition of copper oxide films

Spray parameters	Values
Copper nitrate solution conc	0.1M
Manganese nitrate	calculated amounts (for 0.5at%, 1at% and 2 at%)
Solvent	Distilled water
Substrate temperature	350°C
Carrier gas	Compressed air (~3 kg/cm²)
Angular distance	~25 cm
Rate of spray	4.4 ± 0.1 ml/min
Total spray time	150 sec

Using Ga/In eutectic, silver paint and copper wire, ohmic electrical contact was generated for PEC measurements on the uncoated area (covered by aluminium foil during film deposition) This area was later covered by non-transparent and non-conducting epoxy-resin (Hysol, Singapore). The CuO films, prepared as above were found of p type (as determined by observing Seabeck effect).

3. Structural characterization

The films were characterized using X-Ray Powder Diffractometer (X'PERT Model, Philips, with graphite monochromator) using Cu-Kα wavelength. Figure 1 shows the X-ray diffraction patterns of undoped and 2 at%Mn doped CuO films. Which confirms the polycrystalline nature. The (111), ($\bar{2}$00), (020), (113), ($\bar{2}$20) and (004) peaks of the CuO phase appeared. XRD pattern revealed the shifting of peaks towards higher 2θ in Mn-doped films. This implies that in the crystal structure in-plane expansion is taking place. In the obtained X-ray diffractograms, some peaks corresponding to the underlying SnO_2 coating were also seen.

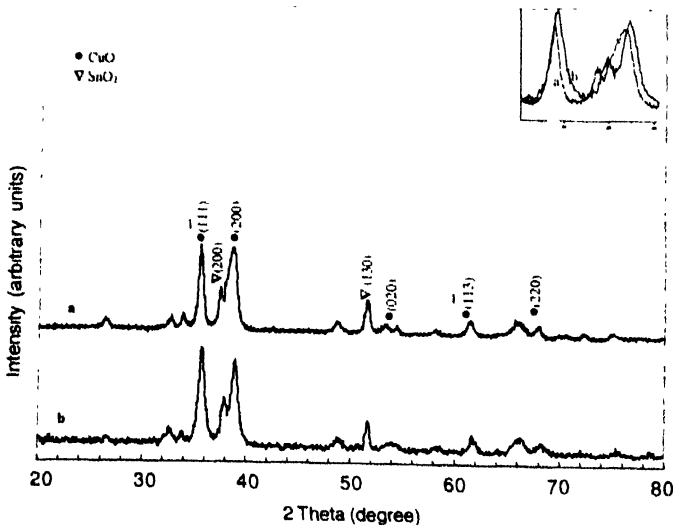

Figure 1. XRD patterns of films deposited at conducting glass : (a) undoped CuO and (b) 2%Mn-CuO.

The surface characterization of films was studied using a Scanning Electron Microscope (Figure 2) and the tentative size of grains/particles formed was determined. The particle/grain size was also calculated from XRD patterns using Scherer's equation . The average size of particles was found to be of the order of ~50 nm.

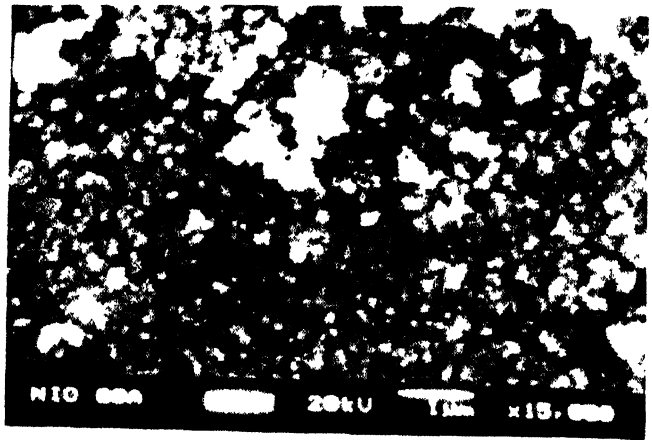

Figure 2. Scanning Electron Micrograph for CuO thin film

4. Band gap measurements

Optical reflection and transmission spectra were recorded for films of cupric oxide deposited at different temperatures The thickness of the films was measured by Telestep method and it was ~1.45 μm. Spectroscopic data were investigated to see the evidence of allowed forbidden transitions between indirect valleys. For a single phonon absorption, the absorption coefficient α for an indirect transitions is given by the equation [15]

$$\alpha = B \frac{\left(h\nu - E_g \pm E_q\right)^n}{h\nu}$$

Here, $n = 2$ for an allowed indirect transitions and $n = 3$ for a forbidden indirect transitions. The -ve sign corresponds to phonon emission and the + ve sign to phonon absorption, B is a constant, E_g is the indirect energy gap and E_p is the energy of the phonon assisting in the indirect transition of the electron. When a plot was made between $(\alpha h\nu)^{1/2}$ and $h\nu$, in the present study a linear graph resulted with the intercept of which $h\nu$ axis gives band gap of material E_g. As shown in the Figure 3 the linear relationship is obtained by plotting $(\alpha h\nu)^{1/2}$ *versus* $h\nu$ The linear sections of the plot indicate an indirect band gap of

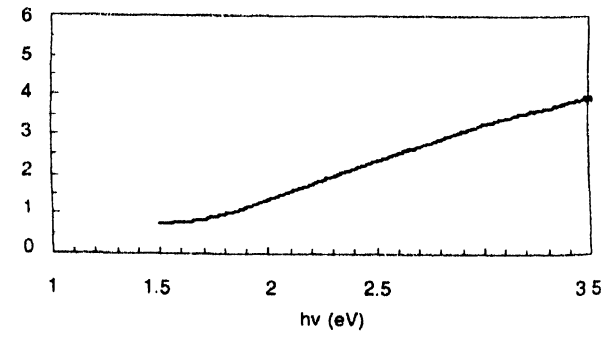

Figure 3. $(\alpha h\nu)^{1/2}$ *versus* $h\nu$ for CuO thin film.

~1.4 eV for thin films. These values fit well with the earlier reported band gap values of CuO [12,13].

5. Photoelectrochemical measurements

The photoelectrochemical measurements involved monitoring of current-voltage (*I-V*) characteristic, under darkness and illumination, using a three electrode system in a glass cell fitted with pyrex glass window to facilitate the transmittance of light to the photoelectrode surface. The CuO thin film electrode (working electrode, surface area of 1.5 cm^2) was used in conjuction with platinum and saturated calomel electrodes (SCE), which were used as counter and reference electrodes, respectively. PEC measurements were performed using a potentiostat (Model ECDA-001, Con-Serv Enterprises) and a 250 W-Xe Lamp (Bentham) was used as light source. The intensity of light was adjusted and fixed at 0.16 W cm^{-2}. The electrolyte used was NaOH.

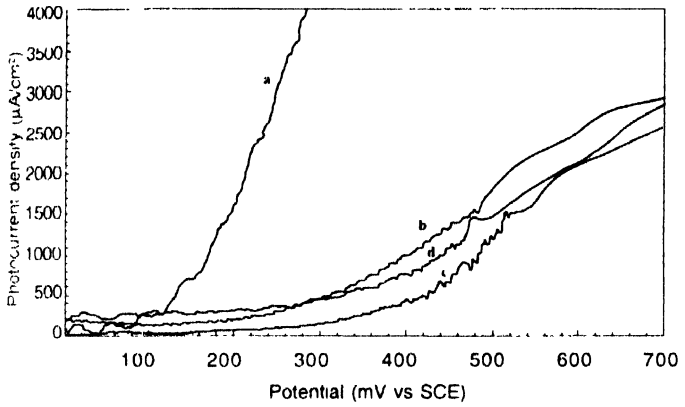

Figure 4(1). Curves of undoped and Mn-doped CuO/SnO_2 electrodes at various doping concentrations (a) undoped, (b) 0.5 at%Mn, (c) 1 at%Mn and (d) 2 at%Mn

It is evident from Figure 4(1) that the photoelectrochemical response in the doped sample is less than the undoped sample. The onset of photocurrent in undoped CuO is at ~120 mV, while in Mn-doped CuO films at ~375 mV. The observed reverse effect of Mn doping on the photoelectrochemical response of the films, can be attributed to the possible neutralization of naturally occurring majority charge carriers (holes) present in undoped copper oxide with the extra electrons furnished by the dopant Mn atoms, particularly, from their d orbitals. The decrease in majority charge carriers is probably adversely affecting the formation of depletion layer at the film-electrolyte junction, which might be responsible for rapid recombination of photogenerated electron-hole pairs. Better photoresponse of CuO films was observed at pH13 as is evident from Figure 4(2).

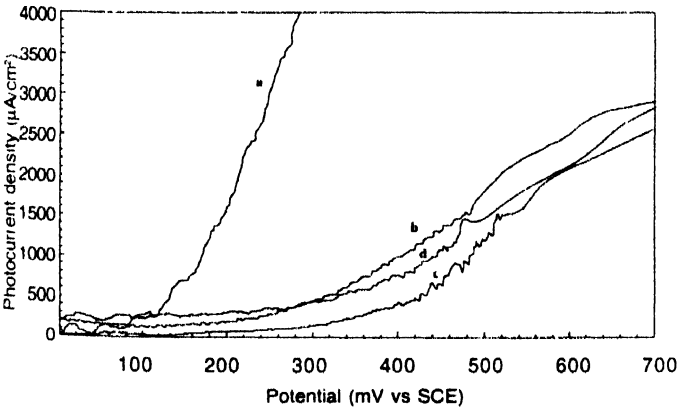

Figure 4(2). Curves of undoped CuO/SnO_2 electrodes at various pH of electrolyte (NaoH) : (a) pH 13 and (b) pH 11.

6. Conclusion

CuO thin films are found to be good candidate for PEC studies. However, exhaustive work is still needed to observe the longevity (*i.e.* life span) of films in contact with electrolyte, particularly, under illumination. Besides, the effect in changes in electrolyte composition on photosensitivity of film and the role of catalysts/sensitizers also need to be investigated. Work on these lines is in progress.

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